# Core and Valence Photoemission Measurements on the CMR materials $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$

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The colossal magnetoresistive (CMR) oxides represent a prototypical type of strongly correlated material that has attracted much attention in recent years [1]. In this class of compounds, electrical resistance is strongly dependent on magnetic order, with possible future applications for example in high-density read heads. In particular, hole-doped manganese oxides with the perovskite structure and the general formula $R_{1-x}A_xMnO_3$, with R being a trivalent rare-earth (here La) and A a divalent cation (Ca or Sr, for our systems), have recently been found to exhibit changes in electrical resistance in magnetic fields that are orders of magnitude greater than those achieved in magnetic multilayer structures of the giant magnetoresistive (GMR) type [2]. The parent compounds $La^{3+}Mn^{3+}O_3$ and $A^{2+}Mn^{4+}O_3$ both have a perovskite structure and are insulators [3]. Between these two end compounds exists a continuous solid solution whose stoichiometry can be denoted $La_{1-x}A_xMnO_3$ and whose structural, magnetic, and transport properties depend sensitively on doping level x. Hole doping causes an insulator-metal transition with a simultaneous onset of metallicity and ferromagnetism [4]. Another peculiar aspect of the CMR materials is the half-metallic nature of the electronic structure, including strong spin polarization of states near the Fermi level [4,5].

The exchange interaction between the localized $t_{2g}$ spins and $e_g$ carriers governs the electronic properties, as usually described in terms of the double exchange (DE) model [6]. Doping of the trivalent rare-earth site by divalent ions causes a corresponding number of $Mn^{3+}$ ions to become $Mn^{4+}$. The displacement of these holes increases the conductivity [7]. In the DE model, the hopping transfer integral for an electron is determined by the degree of alignement of the on-site spins, which is in turn sensitive to the dopant concentration level x. Nevertheless, the emerging theoretical picture is that DE alone cannot account for the large magnetoresistance observed in the CMR compounds. It has been proposed to supplement the DE model with a strong coupling of the electrons to the lattice, resulting in lattice distortions and polaron formation [8]. Moreover, it has recently been suggested that there may be in this class of compounds a substantial degree of $3d^4$ - $3d^4$ ($Mn^{3+}$ - $Mn^{3+}$) charge disproportionation into more stable $3d^5$ - $3d^3$ ($Mn^{2+}$ - $Mn^{4+}$) pairs [9]. Many unanswered questions thus remain concerning the physics of these materials, and these we have begun to address via core and valence photoemission measurements on the newly-commissioned EPU beamline 4.0.2.

We here report preliminary photoemission results obtained from a set of high quality single-crystal CMR samples, namely $La_{1-x}Ca_xMnO_3$ with x = 0.1, 0.2, and 0.3. Other data has been obtained for a similar set of $La_{1-x}Sr_xMnO_3$ samples, but will be reported elsewhere. These data have been taken with the Advanced Photoelectron Spectrometer/Diffractometer [10], which has now been relocated to 4.0.2. We have also developed a method for cleaving such samples in situ (in a pressure better than $10^{-10}$ torr), thus permitting the study of cleaner and better characterized surfaces than has been possible in prior work [5,11].

An overall photoelectron spectrum for a cleaved surface of the cubic CMR material $La_{1-x}Ca_xMnO_3$, with x = 0.2 is shown in Fig. 1a, with various spectral features labelled. The inset shows a higher-resolution spectrum extending from the Fermi level to a binding energy of about
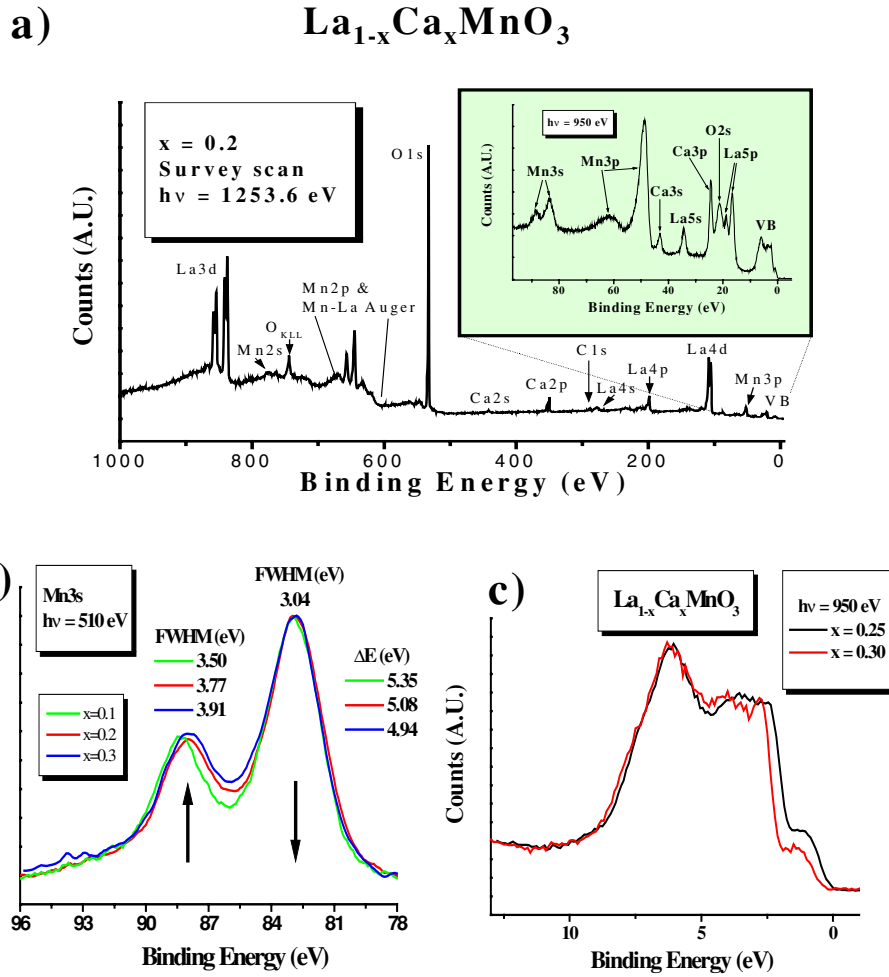
**Figure 1.** Photoelectron spectra from *in situ* cleaved $La_{1-x}Ca_xMnO_3$ samples: a) Overall spectrum for x = 0.2. In the inset, a higher-resolution spectrum extending from the valence bands to about 95 eV binding energy is shown. b) Multiplet-split Mn 3s core level spectra for x = 0.1, 0.2 and 0.3. The dependence on the hole concentration x of the general spectral shape, the doublet separation ΔE, and the width FWHM of the spin-up multiplet peak indicates the sensitivity of such spectra to changes in the relative numbers of $Mn^{3+}$ and $Mn^{4+}$ species. c) Valence bands for x = 0.3 and x = 0.25 taken at 950 eV photon energy.

95 eV, with both the valence-band region and various core levels from all constituent atoms being present. A quantitative analysis of these spectra based on all of the elements present in the material has confirmed the expected stoichiometry and dopant level x, and further shown the initial C contamination just after cleavage to be less than 0.1-0.2 monolayers (note the extremely small C 1s peak in the overall spectrum). Similar results have been found for other samples corresponding to different doping level species and concentrations. Moreover, the carbon contamination does not change significantly, always remaining less than 0.5-1.0 monolayers, even after several hours of measurement, indicating a high surface cleanliness and stability.

In Fig. 1b, we show the Mn 3s core level spectra of the samples corresponding to x = 0.1, 0.2 and 0.3. The Mn 3s core level spectrum shows the expected multiplet splitting, as observed in prior work on less well characterized surfaces and at lower energy resolution [11]: upon emitting an electron from the 3s core level, two final states for the Mn ion are possible, depending upon the coupling of the remaining 3s electron with the 3d valence-band electrons. Such multiplets provide a source of spin-polarized photoelectrons, with the spin-polarization being referenced to the emitter magnetic moment, and not to any laboratory frame [12]; the dominant polarizations

are indicated in Fig. 1b. The multiplet energy separation $\Delta E$ can be qualitatively estimated from $\Delta E = (2S_v + 1)K_{3s\text{-}VB}$, where $K_{3s\text{-}VB}$ denotes the exchange integral between the 3s core level and the valence band and $S_v$ is the net spin in the valence band. The multiplet energy separation therefore permits estimating the local magnetic moment or, in other words, the net spin of the emitter atom. The dependence on the hole concentration x of the peak separation $\Delta E$ indicates the sensitivity of this multiplet to changes in the relative numbers of $Mn^{3+}$ and $Mn^{4+}$ species that are thought to be present in these materials, and should also permit sensing the presence of any $Mn^{2+}$ ions via the disproportionation mentioned previously. In the simplest picture, if hole doping causes a corresponding number of $Mn^{3+}$ ions to become $Mn^{4+}$, the value of the net spin in the valence band should change from $S_v = 2$ to $S_v = 3/2$. It is therefore expected that the multiplet separation should decrease upon doping by divalent ions or, in other words, as x increases. This is in qualitative agreement with our results. On the contrary, the presence of $Mn^{2+}$ species with higher $S_v = 5/2$ would increase the energy separation $\Delta E$, contrary to what we observe. Moreover, the increase of the width (FWHM) of the spin-up peak located on the higher binding energy side and the increase of the spectral weight over the region of about 85-88 eV binding energy upon increasing the dopant level x provide support for the model in which the electronic properties of the CMR materials are governed by the interplay of $Mn^{3+}$ and $Mn^{4+}$ species.

In Fig. 1c are shown two valence spectra for x = 0.25 and 0.30 obtained at high enough photon energies (the so-called XPS limit) to be sampling a matrix-element-modulated density of states, rather than a particular region in **k**-space. These spectra exhibit extreme sensitivity in their fine structure to even this small a change in dopant levels.

Such core and valence photoemission measurements will be extended in the future over the full range of dopant levels, and to involve spin resolution, magnetic circular dichroism, and temperature variation.

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